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An Analysis of Molecular Volumes from the Point of View of the Lewis-Langmuir Theory of Molecular Structure

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AN ANALYSIS OF MOLECULAR VOLUMES FROM THE POINT OF VIEW OF THE LEWIS-LANGMUIR THEORY OF MOLECULAR STRUCTURE.

According to the Lewis[1]-Langmuir[2] theory of valence and atomic and molecular structure, the numbers of electrons surrounding the positive nuclei of the atoms of the inert gases are such as to permit of particularly stable arrangements. The atoms of the other elements enter into combination in such a manner as to group around their respective nuclei, by taking up, losing or sharing electrons, a number of electrons equal to that in the atoms of the inert gas nearest to them in the periodic table.[3] As a result of this tendency the number of electrons about the positive nuclei of atoms of those elements which tend to revert to the *same* rare gas is the same, when the atoms are in combination. Further, it sometimes happens that different atoms or groups of atoms, existing alone as molecules or acting as the nuclear atoms of compounds, have as a whole the same numbers and *arrangements*[4] of electrons and therefore differ only in the magnitude and distribution of the charges on the positive nuclei of the atoms. Such compounds and groups of atoms Langmuir[5] calls "isosteres." Langmuir has pointed out the marked similarity of physical properties of pairs of isosteres which are capable of independent existence as molecules, such as nitrous oxide and carbon dioxide. This being the case, it does not seem improbable that the volumes of isosteric atoms or groups of atoms, whether these exist as free molecules or as the nuclear atoms of a compound, may be the same. This involves the assumption that the outer shells of electrons in isosteres have the same dimensions independent of the charges on the positive nuclei of the atoms or at least that the volume of the molecule as a whole shall behave as if this were the case.[6] The remainder of this paper is devoted to establishing the fundamental correctness of this assumption and to examining the evidence

[1] Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

[2] Langmuir, *ibid.*, **41**, 868 (1919).

[3] It is not to the particular arrangements of electrons in the inert gases that the atoms of the other elements tend to revert, for in organic compounds, for example, the carbon atoms are assumed to have the 8 electrons arranged in pairs at the corners of a tetrahedron, while in neon, the corresponding rare gas, the 8 electrons are at the corners of a cube.

[4] This is always to be understood to refer to all the electrons in the molecule or group of atoms, not merely to those in the outer shell.

[5] Langmuir, *J. Am. Chem. Soc.*, **41**, 1543 (1919).

[6] See note, p. 1001.

furnished by molecular volumes regarding the structure of certain molecules and nuclear atoms.

For the comparisons of molecular volumes the values of the quantity b of van der Waals' equation have been employed. These have been calculated from the relation $b = {}^1/_8 RT_c/p_c = 0.000458\ T_c/p_c$ in which, T_c is the critical temperature in degrees, absolute; and p_c is the critical pressure in atmospheres. The values of the critical temperature and pressure and of b are given in Table I. The results of Young and the recent determinations of Cardoso have been used wherever possible.

TABLE I.—THE VALUES OF CRITICAL TEMPERATURES AND PRESSURES, AND OF VAN DER WAALS' b.

T_c = critical temperature in degrees, Kelvin.
p_c = critical pressure in atmospheres.
$b \times 10^5 = 45.8\ T_c/p_c$.

	T_c. °K.	P_c. Atmospheres.	$b \times 10^5$.	Observers.[1]
Ne	44.7	26.9	76	14
Ar	150.7	48.0	144	8
Kr	210.5	54.3	177	17
Xe	289.7	58.2	228	15
H_2	33.2	12.8	119	14
CH_4	190.2	45.6	191	7
NH_3	406.0	112.3	165	6
H_2O	647.0	217.5	136	10
C_2H_4	282.6	50.7	225	6
O_2	155.0	49.3	144	7
C_2H_2	308.6	61.7	229	6
N_2	128.3	33.7	174	7
CO	134.4	34.6	178	7
NO	180.2	64.6	128	1
CO_2	304.0	72.9	191	6
N_2O	309.6	71.7	198	6
PH_3	324.4	64.5	230	4
H_2S	373.4	89.1	192	6
HCl	324.4	81.6	182	6
C_2H_6	305.2	48.9	286	6
C_3H_8	370	44.0	385	13
n-C_5H_{12}	470.3	33.0	652	18
iso-C_5H_{12}	460.9	32.9	641	18
n-C_6H_{14}	507.9	29.6	785	18
n-C_7H_{16}	539.9	26.9	919	18
n-C_8H_{18}	569.3	24.6	1057	18
$(CH_3)_2CH.CH(CH_3)_2$	500.5	30.7	745	18
$(CH_3)_2CHCH_2$ $CH_2CH(CH_3)_2$	549.9	24.6	1025	18
$(CH_3)_2O$	400.1	53.0	346	5
$(C_2H_5)_2O$	466.9	35.6	600	18
$C_2H_5NH_2$	456.2	55.5	376	3
$(CH_3)_2NH$	437.6	52.4	382	3
$(C_2H_5)_2NH$	496.3	36.6	621	3

[1] Observers:

TABLE I (*continued*).

	T_c. ° K.	P_c. Atmospheres	$b \times 10^5$.	Observers.
Cl_2	414.0	83.9	226	9
	419.0	93.5	205	11
	417.0	76.1	252	16
CCl_4	556.2	45.0	566	18
$GeCl_4$	550.0	38.0	663	12
$SnCl_4$	591.8	37.0	733	18
C_6H_6	561.6	47.9	537	18
C_6H_{12}	553.1	39.8	635	18
$C_6H_5CH_3$	593.7	41.6	653	2
C_6H_5F	559.6	44.6	574	18
C_6H_5Cl	632.3	44.6	648	18
C_6H_5Br	670.0	44.6	687[a]	18
C_6H_5I	721.0	44.6	740[a]	

[a] Calculated by Young.

1. Adwentowski, *Ion*, **2**, 1 (1910); cf. *C. A.*, **4**, 2777 (1910).
2. Altschuel, *Z. physik. Chem.*, **11**, 577 (1893).
3. Berthoud, *J. chim. phys.*, **15**, 3 (1917).
4. Briner, *ibid.*, **4**, 476 (1906).
5. Briner and Cardoso, *ibid.*, **6**, 641 (1908).
6. Cardoso, *J. chim. phys.*, **10**, 470 (1912).
7. Cardoso, *ibid.*, **13**, 312 (1915)).
8. Crommelin, *Comm. Phys. Lab. Leiden*, **115**, 118 (1910).
9. Dewar, *Phil. Mag.*, [5] **18**, 210 (1884).
10. Holborn and Baumann, *Ann. Phys.*, [4] **31**, 945 (1910).
11. Knietsch, *Ann.*, **259**, 100 (1890).
12. Nilson and Pettersson, *Z. physik. Chem.*, **1**, 38 (1887).
13. Olszewski, *Phil. Mag.*, [5] **39**, 188 (1895).
14. Onnes, *Proc. Acad. Sci. Amsterdam*, **20**, 178 (1917).
15. Patterson, Cripps, and Whytlaw Gray, *Proc. Roy. Soc.*, [*A*] **86**, 579 (1912).
16. Pellaton, *J. chim. phys.*, **13**, 426 (1915).
17. Ramsay and Travers, *Phil. Trans. Roy. Soc.*, **197**, 47 (1901).
18. Young, *Sci. Proc. Roy. Dublin Soc.*, N. S. **12**, 374 (1909–10).

Unfortunately, lack of space does not permit an extended discussion of the recent paper of J. J. Van Laar[1] on the additivity of the quantity b of van der Waals' equation. He has assumed arbitrary and sometimes variable values for the volumes of the atoms and obtains good average agreement between calculated and observed values. His atomic volumes are, however, difficult to reconcile with the Lewis-Langmuir theory.

The paragraphs immediately following deal with the molecular volumes of those compounds which contain carbon, nitrogen and oxygen as nuclear atoms.

Methane, Ammonia and Water.—The nuclear carbon, nitrogen and oxygen atoms in methane, ammonia and water, respectively, are isosteric since each consists of a positive nucleus and pair of electrons surrounded

[1] Van Laar, *J. chim. phys.*, **14**, 3 (1916).

by an octet of electrons. If these isosteric nuclear atoms have the same volume, then the differences in volume between pairs of these substances will be the volume of the extra hydrogen atoms one contains over the other. The volumes of the compounds are, methane, 191; ammonia, 165; water, 136. Methane has one more hydrogen than ammonia and is greater by 26 units. Ammonia has one more hydrogen than water and is greater by 29 units. It should be remembered that the errors in the volumes fall on these differences. Taking the average difference of 28 as the volume of one hydrogen atom in these compounds and subtracting for the total number of hydrogen atoms from the volume of each compound, to find the volumes of the nuclear atoms, one obtains for the latter the values

CH_4 : 191–112 = 79
NH_3 : 165–84 = 81 Average 80.
H_2O : 136–56 = 80

The nuclear atoms are seen to have almost exactly equal volumes, substantiating the assumption made.

For neon, the corresponding inert gas, the volume is 76. That the volume of the nuclear atoms in the above compounds is practically the same (80) would seem to indicate that these atoms are essentially cubic, as neon is assumed to be. The tendency of the hydrogen atoms to draw together the pairs of electrons, by means of which they are held, to give the nuclear atom a tetrahedral structure, is apparently not great. That the volume of the nuclear atoms and that of neon are not more nearly equal may be due to slight deformation of the cubic structures in the hydrides or to the inaccuracy of the value for neon, the critical data for which are given by Kammerlingh Onnes as preliminary.

Ethylene and Oxygen.—Elementary oxygen and the carbon atoms in ethylene are isosteric. In both, the positive nuclei (with a pair of electrons each) are surrounded by 12 electrons forming two tetrahedral octets sharing two pairs, that is, meeting along an edge. If the volumes of the two isosteres are the same, the difference in volume between ethylene (255) and oxygen (144) represents the volume of the 4 hydrogen atoms in ethylene. One-fourth of this difference should be the volume of one hydrogen.

$$\frac{V_{C_2H_4} - V_{O_2}}{4} = \frac{255 - 144}{4} = 28.$$

The volume of one hydrogen is found to be 28 as in methane and the like.

Acetylene, Nitrogen and Carbon Monoxide.—For reasons to be discussed later, nitrogen and carbon monoxide are assumed to have the normal, acetylenic, rather than the condensed structure suggested by Langmuir. Thus, nitrogen, carbon monoxide, and the carbon atoms of

acetylene are isosteric, since the structure for all consists of two positive nuclei (with a pair of electrons each) surrounded by two tetrahedral octets composed of 10 electrons, 3 pairs being shared, that is, meeting face to face.

The volumes of nitrogen and carbon monoxide are 174 and 178, respectively, that of the unsymmetrical carbon monoxide being slightly the greater. Taking symmetrical nitrogen to compare with the symmetrical carbon atoms of acetylene (229), it is found that one-half the difference between the volumes of the two compounds, which should equal the volume of one hydrogen atom, is again 28.

$$\frac{V_{C_2H_2} - V_{N_2}}{2} = \frac{229 - 174}{2} = 28.$$

It is convenient to point out here that the volumes of carbon dioxide and nitrous oxide, which are isosteric, are 191 and 198, respectively. If nitrous oxide has the structure N=N=O, as Langmuir is inclined to think, then again the unsymmetrical isostere (N_2O) has slightly the greater volume, as found in comparing carbon monoxide and nitrogen. The lack of symmetry in both cases is in the distribution of positive charge among the nuclei of the atoms.

Elementary fluorine is isosteric with the nuclear carbon atoms of ethane. As, however, the critical constants of the former have not been determined, no comparison can be made. It will be of interest to obtain a value for two tetrahedral neon octets sharing one pair, as in ethane. This can be done by subtracting 6 × 28 for 6 hydrogens from the value for ethane (286); thus 286 — 168 = 118 for the nuclear C—C atoms.

Summary.—From the above it results that with one value (28) for hydrogen, 80 for the cubic neon structure, 144 for 2 tetrahedral neon structures sharing 2 pairs and 174 when sharing 3 pairs, the volumes of methane, ammonia, water, ethylene, acetylene, carbon monoxide, oxygen and nitrogen can be reproduced as follows.

	Observed.	Calculated.	Δ.	Van Laar calc.	Δ.
CH_4	191	192	+1	156	—35
NH_3	165	164	−1	162	—3
H_2O	136	136	0	138	+2
O_2	144	(144)[a]	...	140	—4
C_2H_4	255	256	+1	256	—1
N_2	174	(174)[a]	...	170	—4
C_2H_2	229	230	+1	228	—1
CO	178	174	−4	170	—8

[a] Assumed in the calculation.

The calculated values agree with the observed within 0.5% with the exception of that for carbon monoxide, which is about 2% too low.

The results obtained in the foregoing analysis are taken to be good evidence of the correctness of the assumption that isosteres, whether

existing alone as molecules or forming the nuclear atoms of hydrides have the same volume, independent of the particular atoms involved. It is very unlikely that all the relations cited above—namely, that the volumes of methane, ammonia and water can be expressed with one value for all the nuclear atoms and another for hydrogen, or that this same value for hydrogen and the values for elementary oxygen and nitrogen can express the volumes of ethylene and acetylene, respectively—are simply fortuitous. It is true that Van Laar, making different assumptions, finds nearly as good agreement, with the exception of his value for methane, which is seriously in error (156 calculated; 191 observed). In order to get this agreement, however, he requires two values for hydrogen, two for nitrogen and one each for carbon and oxygen. In the present analysis, one value is used for hydrogen and three different values are assigned to the three different arrangements of electrons about the nuclear atoms met with in these compounds.

Effect of Multiple Bonds.—For ethane, ethylene and acetylene, Van Laar uses a single value each for carbon and hydrogen, in effect assuming that the differences in volume among these compounds depend wholly upon the number of hydrogen atoms in the different molecules. The results recorded in this paper indicate that there is, in addition, a difference due to the manner in which the carbon atoms are combined, that is to say, a difference due to the type of electron structure. Expressed in terms of the volume of a single atom, the values for a single neon octet combined in the various ways are: sharing no pairs (CH_4, etc.) 80; sharing one pair (C_2H_6) 59 (118/2); sharing two pairs (O_2 and C_2H_4) 72 (144/2); sharing three pairs (N_2 and C_2H_2) 87 (174/2).

When one pair is shared, the volume is one-quarter less (59/80 = 74%) than when no pairs are shared. The similarity between the volumes of the nuclear atoms in methane, etc. (when no pairs are shared with other octets) and that of neon was taken to indicate that the nuclear atoms in the former are nearly cubic. In ethane, the nuclear atoms are almost certainly tetrahedral. The ratio of the volumes probably represents, therefore, the relation between the volumes of the cubic octet and the tetrahedral octet of neon.

When 2 pairs are shared, the volume of a single atom is 13 units greater than when one pair is shared and when 3 pairs are shared, there is a further increase of 15 units per atom. The distances between the centers of two tetrahedra meeting (*a*) at their apexes (*b*) along an edge (*c*) at a face, are in the ratio, 4 : 3 : 2. These configurations correspond to the sharing of one, two and three pairs, respectively. Thus, the tendency, if unresisted, on sharing 2 and 3 pairs would be to bring the positive nuclei at the centers of the tetrahedral electron shells nearer and nearer together. The volume in-

creases on sharing successively the second and third pairs probably represent the reaction of the positive nuclei against this tendency. By attempting to get as far apart as possible they distend the molecule. This state of tension due to the multiple bond is evidently an element of weakness and the multiple bond might be expected to be a seat of chemical activity, as is known to be the case.

Structure of Nitrogen.—Langmuir accounts for the inertness of nitrogen and carbon monoxide by assuming a condensed structure consisting of the 2 positive nuclei each holding a pair of electrons (corresponding to helium) and holding between them a third pair, this structure being surrounded by 8 electrons at the corners of a cube. The alternative structure consists of 2 octets sharing 3 pairs, as do the carbon atoms in acetylene. As the reactivities of nitrogen and carbon monoxide are not so great as that of acetylene, Langmuir is inclined to think the structures cannot be similar. Reactivity is, however, a rather vague term. It is true that nitrogen is commonly spoken of as inert and acetylene as active chemically. Yet if the strength of the bond joining the nuclear atoms be measured by the tendency of the two compounds to dissociate, the one into nitrogen atoms and the other into CH radicals, the *stabilities* must certainly be assumed to be of the same order.

As pointed out in the first part of this paper, there is good evidence that the volumes of elementary nitrogen and the two carbon atoms of acetylene are the same, thus indicating a similarity in structure. Furthermore, one would expect such a very condensed structure as Langmuir suggests for nitrogen, the outermost electrons of which form only a single octet, to have a decidedly smaller volume than elementary oxygen, for example, the outer shell of which consists of two octets of electrons sharing two pairs; or of argon, which consists of a single positive nucleus (but with a positive charge of 18), a pair of electrons and two octets of electrons one outside the other. Actually, the volumes of elementary oxygen and of argon are both 144, while that of elementary nitrogen—174—is decidedly larger than either.

The fact that the volume of elementary nitrogen is greater than that of elementary oxygen also has a bearing on the general assumption made in this paper, that it is principally the particular arrangement of electrons rather than the charge on the positive nuclei which determines the volume of an atom or group of atoms. Since the positive nuclei of oxygen atoms possess a charge of +8 while that of the nitrogen atoms is +7, one might have expected that the greater repulsion between the larger nuclei of oxygen would have given to elementary oxygen the greater volume. That it is distinctly less in volume than is elementary nitrogen, with +7 positive nuclei, indicates that the volume is more influenced by other factors. The other apparent difference between the compounds, accord-

ing to the theory, being in the number and arrangement of the electrons—the limiting boundaries of the molecules—it is reasonable to refer the volume relation rather to this.

Nitric Oxide.—Nitric oxide is peculiar in having an odd number of electrons (15). It is thus intermediate between elementary nitrogen with 14, and elementary oxygen with 16 electrons. Langmuir has suggested that it may have essentially the structure which he assigns to elementary nitrogen, the extra, odd electron being "imprisoned in the octet comprising the shell." As this structure for nitrogen has been rendered doubtful by the preceding considerations it will be of interest to find what other structure is possible and what are the indications furnished by the volume of the substance.

The volume of nitric oxide is surprisingly small, 128, that of oxygen being 144 and nitrogen, 174. It is in fact actually nearer that of the carbon atoms in ethane (118). Nitric oxide contains one more electron than nitrogen and it is possible that in the former the octets, like those in nitrogen, share 3 pairs, the odd electron being at the center of the triangle formed by these 3 pairs, directly between the 2 positive nuclei and held in place by the attraction of the latter. The odd electron so placed would certainly tend to draw the nuclei together, lessening the distention of the molecule and making the volume of the molecule less than that of elementary nitrogen. Actually the volume is reduced nearly to the normal volume of 2 octets sharing a single pair as exemplified by the carbon atoms in ethane. In the latter case the shared electron pair is also placed directly between the 2 positive nuclei.

The odd electron placed as suggested above would certainly be held under rigid constraints. Lewis,[1] who would attribute color in compounds to weakly held electrons, has pointed out that of the substances containing an odd number of electrons, only nitric oxide is colorless, that is to say, all the electrons including the odd are rigidly held.

Hydrocarbons, Amines and Ethers.—There are a few hydrocarbons, amines and ethers for which data are available whose chains of nuclear atoms are isosteric and should, therefore, have equal volumes. A comparison of the 5- and 3-atom chains is given below. The volumes of the chains have been obtained by subtracting 28 for each hydrogen atom from the volumes of the compounds. It should be borne in mind that this method throws all the experimental error on the volume of the chain.

5-Atom chains.		3-Atom chains.	
	$b \times 10^5$. 28 H. Chain.		$b \times 10$. 28 H. Chain.
n-C_5H_{12}	652 — 336 = 316	C_3H_8	385 — 224 = 161
$(C_2H_5)_2NH$	621 — 308 = 313	$C_2H_5NH_2$	376 — 196 = 180
$(C_2H_5)_2O$	600 — 280 = 320	$(CH_3)_2NH$	382 — 196 = 186
		$(CH_3)_2O$	346 — 168 = 178

[1] *Loc. cit.*

With the exception of the value obtained from propane, the agreement is satisfactory within each series.

Hydrocarbon Chains.—As is well known, the volumes of compounds containing long chains of carbon atoms are not strictly additive. The values for the increment CH_2 usually rise in ascending a series. This is true of the values of b for the straight-chain hydrocarbons, as will be seen from the following comparison of observed values with those calculated from the values H = 28 and C = 59 (as found in ethane).

	Observed.	Calc.		%
C_2H_6	286	(286)	..	...
C_3H_8	385	401	16	4.2
n-C_5H_{12}	652	631	21	3.2
n-C_6H_{14}	785	746	39	5.0
n-C_7H_{16}	919	861	58	6.3
n-C_8H_{18}	1057	976	81	7.7
$(CH_3)_2CH.CH_2CH_3$	641	631	10	1.6
$(CH_3)_2CH.CH(CH_3)_2$	745	746	1	0.1
$(CH_3)_2CH.CH_2CH_2CH(CH_3)_2$	1025	976	49	4.8

For the straight chain compounds, the percentage by which the observed values exceed the calculated steadily increases, with increasing number of atoms.

The branched chain isomers have volumes smaller than the straight chain and therefore nearer the calculated values. It is of interest to note that that compound in which the relative amount of departure from the straight chain is greatest, namely, di-*iso*-propyl, $\begin{matrix} CH_3 & & CH_3 \\ & \diagdown\!\diagup & \\ & CH.CH & \\ & \diagup\!\diagdown & \\ CH_3 & & CH_3 \end{matrix}$, has a volume almost identical with that calculated (745 observed; 746 calculated).

Ring Structures.—It is of interest to find what values are obtained for ring structures. The value for toluene will first be examined. The radical, C_6H_5, should have a volume equal to that of benzene less one hydrogen atom or 537 — 28 = 509. The volume of CH_3 should be 59 + (3 × 28) = 143. The sum of these gives the value for toluene, $C_6H_5CH_3$, 652. The observed value is 653.

For the rings in benzene and cyclohexane, the following values are obtained by subtracting for the total number of hydrogen atoms: C_6H_6, 537 — (6 × 28) = 369; C_6H_{12}, 635 — (12 × 28) = 299.

The unsaturated benzene ring has the greater volume. This is in agreement with the relations already found between the volumes of saturated and unsaturated nuclear atoms. The carbon atoms in cyclohexane might have been expected to have the volume 59 each. Actually the volume is 299/6 = 50. The ring structure appears to be very much condensed.

Phosphine and Hydrogen Sulfide.—Data are not available for enough compounds having nuclear atoms related to argon, as those just discussed are related to neon, to allow very satisfactory comparisons to be made. There are dependable values for phosphine, hydrogen sulfide and hydrogen chloride, however, and these will be analyzed so far as possible.

If, as in the case of methane, ammonia and water, the difference between the volumes of phosphine and hydrogen sulfide (230 — 192 = 38) be taken as the volume of one hydrogen in these substances, then for the volumes of the nuclear atoms, one obtains: PH_3, $230 - (3 \times 38) = 116$; H_2S, $192 - (2 \times 38) = 116$. Because of the method of treatment the value for the nuclear atom is necessarily the same in both cases. This value (116) is 116/144 or 80% of that of the corresponding rare gas, argon. A carbon atom in ethane sharing one pair (and in the tetrahedral form) has a volume 59/76, or 78% of that of the corresponding cubical atom, neon. As the volumes of the nuclear atoms in phosphine and hydrogen sulfide bear nearly the same numerical relation to that of the corresponding cubic atom, argon, it would appear that already in the simple hydrides the nuclear atoms related to argon are tetrahedral. The hydrogen atoms by their attraction for pairs of electrons appear to have been able to deform the argon (cubic) structure to such an extent that it is essentially tetrahedral. As the volume of argon is nearly twice that of neon (144, 76) one might have expected this relatively greater deformation of the former structure.

Volume of Hydrogen.—The volume of hydrogen in these compounds appears to be greater than in those compounds containing nuclear atoms related to neon. This is undoubtedly the effect of the very much larger charge on the positive nuclei of atoms related to argon. The hydrogen atom in each of these compounds actually consists only of a singly charged positive nucleus of exceedingly small volume held by means of an electron pair of the nuclear atom but repelled by its positive nucleus. Its contribution to the volume therefore, depends on the equilibrium position it holds with respect to the electron pair and positive nucleus of the nuclear atom. If it is forced out, its apparent volume will be greater and *vice versa*. The hydrogen atom cannot be expected, therefore, to have a constant volume. This is emphasized by the fact that in the elementary state ($b = 119 \times 10^{-5}$), the atom has the relatively very great volume of 60. The greater apparent volume of hydrogen in hydrogen sulfide as contrasted with that in water is indicative of the greater ease of ionization of the former compound—the hydrogen nucleus is normally separated from the nuclear atom to a greater extent. It may be pointed out here that Van Laar's values of 14 for hydrogen combined with carbon and 34 for hydrogen combined with any other atom, are not so easily explained. Although carbon is a very peculiar element, it is

not so markedly different from all other elements, on the basis of the theory, as to lead one to expect any such distinction between the volume of hydrogen associated with it and associated with any other element. One would rather expect either a different value for hydrogen combined with each element or compound, increasing with increasing atomic weight of the element or else for each rare gas type of nuclear atom, as apparently is the case.[1]

Hydrogen Chloride.—The treatment of the value for hydrogen chloride presents certain difficulties. One is prepared to find a structure rather different from any of those so far considered because of the strongly polar nature of the compound. The value (182) is clearly relatively greater than that of hydrogen sulfide, since with one less hydrogen, the value is only 10 less (192, 182). If 38, the value for hydrogen in phosphine and hydrogen sulfide be subtracted from the hydrogen chloride value, the remainder ($182 - 38 = 144$) is precisely the value of argon itself. The chlorine atom in hydrogen chloride thus appears to have the cubic structure, one hydrogen being insufficient to force the atom into the tetrahedral form. This is, of course, just the form (*i. e.*, cubic) which the halogen and alkali atoms are supposed to have in alkali halide crystals, the alkali halides being also highly polar. The assumption of the cubic argon structure by the chlorine atom in hydrogen chloride may serve in some degree to account for the difference in properties between hydrogen chloride and hydrogen sulfide.

Chlorine.—The various determinations of the critical constants for elementary chlorine are, unfortunately, widely divergent. The values for $b \times 10^{+5}$ are 226 (Dewar) 205 (Knietsch, 1890) and 252 (Pellaton, 1915), giving the values 113, 103 and 126 for one chlorine atom. Van Laar chooses to take Dewar's value (113), which is not far from that found here for the nuclear atoms in phosphine and hydrogen sulfide (116). The latter were assumed to be more nearly tetrahedral. Two octets sharing one pair with no combined hydrogen atoms may not be tetrahedral, however. Undoubtedly the attraction of the 2 positive nuclei will tend to draw the shared electrons toward the line joining the nuclei, thus deforming the cubic structure, and the volume of the molecule will at least be less than that of 2 cubic structures with volume 144 (argon) each. Pellaton's recent value of 126 for each atom in elementary chlorine seems best to fulfil the requirements, since it is midway between that of the

[1] It is possible that the apparent volume of the hydrogen atom does increase slightly as the charge on the positive nucleus of the nuclear atom increases but that this is offset by the fact that the electron shell about the nuclear atom *decreases* slightly in volume with increasing nuclear change—the electrons are displaced inward somewhat. It is, in fact, possible to get slightly better agreement assuming a slight regular increase in volume for hydrogen and decrease in volume for the nuclear atom with increase in charge on the positive nucleus of the nuclear atom, in any given series.

tetrahedral atoms in phosphine and hydrogen sulfide (116) and that of the cubic atom, argon (144), corresponding to a deformed cube structure.

Atoms Similar to Krypton and Xenon.—It is not possible to make an analysis of the volumes of compounds containing nuclear atoms related to krypton and xenon because critical data have only been determined for one or two. Since, according to Langmuir, the outer shell of these atoms is made up of 18 instead of 8 electrons, one cannot apply the results already arrived at to the examination of these few compounds. There are, however, two series of compounds the volumes of which yield interesting results. These are the tetrachlorides of carbon, germanium and tin and fluoro-, chloro-, bromo- and iodobenzene.

The Tetrachlorides of Carbon, Germanium and Tin.—If the carbon atom in carbon tetrachloride (566) be taken to be tetrahedral (59), as it almost certainly is, since it shares all four pairs, there is obtained for the volume of one chlorine ((566 — 59/4) = 127). This is very close to Pellaton's recent value for one chlorine atom in elementary chlorine (126). If 127 be taken as the volume of one chlorine in germanium and tin tetrachlorides, one obtains for the volume of germanium and tin $GeCl_4$, 663—507 = 156 = Ge; $SnCl_4$, 733—507 = 226 = Sn. The volumes of the corresponding rare gases are krypton 177, and xenon, 228. The value for tin (226) is close to that of the corresponding rare gas, xenon (228), indicating that the shell of 18 electrons has not been greatly deformed. As the electrons are probably closer together than in the shell of chlorine, it is not impossible that the chlorine might be deformed cubic and the tin atom still have essentially the structure of the rare gas, xenon. The value for germanium (156) is somewhat less than that of the rare gas, krypton (177), to which it corresponds. This would seem to indicate some deformation. However, of the two, greater weight must be attached to the value for tin, since the constants for tin tetrachloride are those of Young while the constants of germanium tetrachloride were determined by Nilson and Petterson (1887) and represent, so far as known, the only determinations of critical constants published by these authors.

A new determination of the critical constants of germanium tetrachloride and a determination of those of silicon tetrachloride would be of great value in this connection.

The Aromatic Halogen Compounds.—The value for benzene is 537. Subtracting 28 for one hydrogen, the value 537—28 = 509 is obtained for the phenyl radical, C_6H_5. If this value be subtracted from those of the aromatic halogen compounds, the remainder should be the volume of the halogens: C_6H_5F, 574—509 = 65 = F; C_6H_5Cl, 648—509 = 139 = Cl; C_6H_5Br, 687—509 = 178 = Br; C_6H_5I, 740—509 = 231 = I.

For fluorine, a value between 59 (tetrahedral) and 80 (cubic) was to

have been expected. The value found is 65. For chlorine, the value 126 was looked for. Actually a value (139) somewhat nearer that of argon (144) was obtained. For bromine (178) and iodine (231), values close to those of the corresponding rare gases, krypton (177) and xenon (228) are obtained, as in the case of tin in tin tetrachloride. As bromine and iodine each share with the radical only one pair out of 18 electrons, one would certainly not expect any great deformation, and little apparently occurs.

Volumes of the Rare Gasses.—According to Langmuir,[1] "the electrons in *any given atom* are distributed through a series of concentric shells, all of equal thickness. Thus, the mean radii of the shells form an arithmetic series, 1, 2, 3, 4....." These shells contain 2 sets of electrons. Thus in xenon, the first shell contains the 2 electrons corresponding to helium, the second shell contains the 2 octets of electrons corresponding to the outermost electrons of neon and argon, respectively, and the third shell contains the 2 sets of 18 electrons, one outside the other, corresponding to the outermost electrons of krypton and, finally, xenon itself. It is specifically stated that this relation of the radii of the shells holds only for one given atom. It will, however, be of interest to see if any such simple relation holds for different atoms.

If the radii are in the ratio 1 : 2 : 3, the mean volumes of the shells must be as 1 : 8 : 27. If the mean volume of a given shell is the same in every atom which contains it, then it might be expected that the mean of the volumes of neon and argon, representing the second shell (helium accounts for the first) and of krypton and xenon, representing the third shell, would be to each other as 8 : 27. The values actually obtained are $(76 + 144)/2 = 110$; and $(177 + 228)/2 = 202.5$. The mean of the volumes of neon and argon is 110, that of krypton and xenon, 202.5. These are clearly not in the ratio required. In krypton and xenon, it is quite possible that because of the larger charge on the positive nucleus, the electrons of the second shell will be drawn inward more than the corresponding electrons in neon and argon and the mean volume of the shell be enough smaller than in neon and argon to satisfy the relation.[2]

[1] THIS JOURNAL, **41**, 932 (1919).

[2] It is of interest to note that the volumes of the rare gases are roughly proportional to the square roots of their atomic weights as will be seen from the following table.

	b.	At. wt.	$\sqrt{\text{At. wt.}}$	$\frac{b}{\sqrt{\text{At. wt.}}}$
Ne	76	20	4.47	17.0
A	144	40	6.32	22.8
Kr	177	83	9.11	19.4
Xe	228	130	11.4	20.0

In fact, rough average agreement can be obtained for molecular volumes (in general) if they are assumed to be proportional to the sum of the square roots of the atomic weights of the constituent atoms.

Two facts, in particular, are brought out by the foregoing analysis. First, isosteric atoms, molecules and groups appear to have the same volume regardless of the particular kinds of atoms of which they are composed. In other words, the number and arrangement of electrons in the outer shells of atoms or groups of atoms is the predominating factor in determining their volume. Second, the volumes of other atoms, particularly of the more complex ones, are intimately related to the volumes of the rare gases.

It is realized that the possibilities of the method of treatment used in this paper are by no means exhausted and the writer expects at some future time to consider further the implications of the present work.

Summary.

1. An analysis of molecular volumes, as determined from the critical data, has been made from the point of view of the Lewis-Langmuir theory and especially of Langmuir's theory of isosteres.

2. Evidence has been brought forward to show that isosteric molecules and nuclear atoms in hydrogen compounds have the same volume. The volume depends, therefore, on the number and arrangement of electrons surrounding the positive nuclei of the atoms rather than on the charges on the nuclei, that is to say, on the particular kinds of atoms concerned. Thus, it has been shown that the nuclear carbon, nitrogen and oxygen atoms of methane, ammonia and water, respectively, have the same volume.

3. It has been shown that the carbon atoms in ethane, ethylene and acetylene have volumes increasing with the degree of unsaturation. The same observation holds in comparing the carbon atoms in benzene and cyclohexane. The volumes of atoms thus increase with the number of electron pairs shared. An explanation of this has been presented.

4. It has been shown that elementary nitrogen and carbon monoxide probably have the normal or acetylenic structure, 3 pairs being shared, rather than the condensed structure suggested by Langmuir.

5. A structure for nitric oxide has been suggested and evidence in its favor produced.

6. The volumes of the rare gases have been considered from the point of view of Langmuir.

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